

REMARKS

Claims 1-12 and 14-16 are pending in the present application.

The rejections of: (a) Claims 1-13 under 35 U.S.C. §103(a) over Kanekiyo et al in view of Kaneko et al, and (b) Claims 1-13 under 35 U.S.C. §103(a) over Satou et al in view of Kanekiyo et al and Kaneko et al, are respectfully traversed.

Magnet powder of the present invention surely aims to suppress oxidation and deterioration of a bonded magnet. However, the present invention does not directly achieve such aim by coating a surfactant on the surface of magnet powder.

The main points of the present invention are as follows:

(1) Object

First, the present invention flows from the fact that cobalt-less R1 d-HDDR coarse powder made of d-HDDR anisotropic magnet powder is used as main magnet powder.

① A bonded magnet made of d-HDDR anisotropic magnet powder has excellent magnetic properties. On the other hand, a bonded magnet has an object that it is easily oxidized and degraded.

According to the present inventors' research, such oxidization and degradation occurs due to "fracture" of particles which constitute the d-HDDR anisotropic magnet powder because a new fracture face generated at the fractured portion is very easy to be oxidized.

Furthermore, d-HDDR anisotropic magnet powders often have cracks in grains or grain boundary due to a method of producing the same such as hydrotreatment. So, the above "fracture" is very easily generated.

Thus, d-HDDR anisotropic magnet powder has extremely high sensitivity to fracturing. (See "Rare-Earth Iron Permanent Magnets", **submitted herewith**; especially, descriptions highlighted on pages 348-353 and 361-365, Fig. 7.20)

② On the contrary, Kanekiyo et al (US 6, 814, 776) and Kaneko et al (JP2000-3809) are based on the fact that a rapid-cooling magnet powder produced by a melt spinning method and a strip cast method is used. However, the rapid-cooling magnet powder is not subjected to hydrotreatment. Therefore, it has no internal cracks, and it is very hard to be fractured (namely, it has low sensitivity to fracturing).

So, the rapid-cooling magnet powder doesn't have an object caused by d-HDDR anisotropic magnet powder, which is a specifically claimed feature of the present invention.

Therefore, the present invention is different from the cited references (Kanekiyo et al and Kaneko et al) on the basis of the magnetic powder used therein.

To the extent that claimed invention differs from the disclosure of Kanekiyo et al and Kaneko et al based on product-by-process limitations, which the Examiner considers to be inherent to the term “d-HDDR”, the courts have enunciated that: “Even though product-by-process claims are limited by and defined by the process, determination of patentability is based on the product itself. The patentability of a product does not depend on its method of production. If the product in the product-by-process claim is the same as or obvious from a product of the prior art, the claims is unpatentable even though the prior product was made by a different process.” *In re Thorpe*, 227 USPQ 964 (Fed. Cir. 1985).

There are two important aspects to the foregoing. First, the products must be identical or an obvious variant thereof. Second, patentability of a product may not depend on its method of production, but the method of production cannot be disregarded if that method provides a distinct structure or product. Indeed, the Board and the Courts have said as much, which is set forth in MPEP §2113 in relevant part:

“The structure implied by the process steps should be considered when assessing the patentability of product-by-process claims over the prior art, especially where... the manufacturing process steps would be expected to impart distinctive structural characteristics to the final product. See, e.g. *In re Garnero*, 412 F.2d 276, 279, 162 USPQ 221, 223 (CCPA 1979)... The

Board stated that the dispositive issue is whether the claimed factor exhibits any unexpected properties compared with the factor disclosed by the prior art.” (citing *Ex parte Gray*, 10 USPQ2d 1922 (Bd. Pat. App. & Inter. 1989))

The foregoing is particularly relevant to the present application. As stated above, the method disclosed by Kanekiyo et al and Kaneko et al is distinct from a hydrotreatment method. Further, for the reasons set forth above, the resultant product from the method disclosed by Kanekiyo et al and Kaneko et al is distinct from that of the presently claimed invention. Accordingly, Applicants submit that Kanekiyo et al and Kaneko et al fail to render the presently claimed invention obvious.

③ The Examiner appears to understand that an intention of the present invention is a method for producing d-HDDR anisotropic magnetic powder. However, Applicants respectfully submit that this “understanding” is a misunderstanding. The present inventors have paid attention to the object which is extracted from d-HDDR anisotropic magnet powder, which is an assumption of the present invention, and have provided a means for solving the object.

(2) Means

① In the present invention, while achieving the above object (to prevent fracture of cobalt-less R1 d-HDDR coarse powder), in order to maintain high magnetic properties as a bonded magnet, resin and specific R2 fine magnet powder comprising anisotropic magnet powder having excellent magnetic properties are mixed in the desired ratio.

While forming the bonded magnet, first of all, the resin and the R2 fine magnet powder which is dispersed in the resin firstly appear as a ferromagnetic fluid layer. The ferromagnetic fluid layer prevents that cobalt-less R1 d-HDDR coarse powder having high sensitivity to fracturing is directly contacted to be fractured.

Then, after forming the bonded magnet (after curing the resin), the resin and the R2 fine magnet powder envelope the cobalt-less R1 d-HDDR coarse powder to be a ferromagnetic buffer for the cobalt-less R1 d-HDDR coarse powder. The ferromagnetic buffer prevents that the cobalt-less R1 d-HDDR coarse powder is directly contacted to be fractured by impact or vibration applied to the bonded magnet.

② In the present invention, both of the cobalt-less R1 d-HDDR coarse powder and the surface of the R2 fine magnet powder are covered by a surfactant in order to improve the fluidity of each magnet powder in the ferromagnetic fluid layer appeared while forming the above bonded magnet, and to prevent the stress and the like causing the fracture from acting on the cobalt-less R1 d-HDDR coarse powder.

Therefore, the coating of the surfactant doesn't directly aim to prevent oxidization of the magnet powder.

③ In the present invention, the grain diameter and the shape (aspect ratio) of the R2 fine magnet powder are limited in order to improve the above fluidity to exhibit the effect for buffering the cobalt-less R1 d-HDDR coarse powder.

④ As for aspect ratio, denominator and numerator in the aspect ratio (large diameter/small diameter) of Kanekiyo et al are reversed with each other in the aspect ratio (small diameter/large diameter) of the present invention.

A first iron-based rare-earth alloy powder having an average grain diameter of 10 μm or more and 70 μm or less and an aspect ratio of 0.4 or more and 1.0 or less in Kanekiyo et al corresponds to the R2 fine powder of the present invention. The grain diameter (10-70 μm) of the first iron-based rare-earth alloy powder is remarkably different from the grain diameter (1-10 μm) of the present invention.

As the Examiner pointed out, Kanekiyo et al refers to the fluidity while forming the bonded magnet, but he merely pointed out from the viewpoint of forming efficiency. As

aforementioned, the present invention brings the fluidity of the magnet powder into question from the viewpoint of preventing the flucture of the cobalt-less R1 d-HDDR coarse powder having high sensitivity to flucturing. Such difference of each viewpoint appears in the above difference of each grain diameter.

⑤ Satou et al (JP6-132107) proposes a composite rare earth bond magnet in which two different kinds of magnet powders having different grain diameter are combined. However, the purpose of Satou et al is to merely improve the magnetic properties, and Satou et al does not pay attention to the above-mentioned object of the present invention. In addition, Satou et al never discloses the surfactant or the aspect ratio which are disclosed in the present invention.

In view of the foregoing, Applicants submit that even if the skilled artisan had each of Kanekiyo et al, Kaneko et al, and Satou et al in hand, the present invention would not be obvious.

As such, Applicants request withdrawal of these grounds of rejection.

The rejection of Claim 7 under 35 U.S.C. §112, second paragraph, is obviated by amendment. Applicants have amended Claim 7 herein to specifically address the Examiner's criticisms. Withdrawal of this ground of rejection is requested.

The rejection of Claim 13 under 35 U.S.C. §101 is obviated by cancellation of this claim. Withdrawal of this ground of rejection is requested.

The objection to Claims 7 and 10 is obviated by amendment. Applicants have amended the claims to address the Examiner's specific criticisms. Withdrawal of this ground of objection is requested.

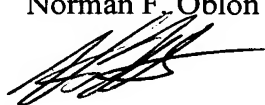
The objection to the specification is obviated by amendment. Applicants have amended the specification, as appropriate, to address the Examiner's specific criticisms. Withdrawal of this ground of objection is requested.

Finally, Applicants respectfully request that the obviousness-type double patenting rejection of Claims 1-13 over Claims 1-15 of US 10/509,687 be held in abeyance until an indication of allowable subject matter in the present application. If necessary, a terminal disclaimer will be filed at that time. Until such a time, Applicants make no statement with respect to the propriety of this ground of rejection.

Applicants submit that the present application is in condition for allowance. Early notification to this effect is respectfully requested.

Respectfully submitted,

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6

Rare-Earth Iron Permanent Magnets

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Rare-earth Iron Permanent Magnets

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Contents

List of Contributors	xvii
Units	xviii
1 Introduction <i>J. M. D. Coey</i>	1
A. Basic concepts	1
1 B, H, and M	2
2 External fields	5
B. Atomic-scale magnetism	10
1 Magnetic moments	10
2 Exchange interactions	15
3 Anisotropy	17
4 Modelling the interactions	23
C. Intermetallic compounds	27
D. Magnets	34
1 Processing	35
2 Micromagnetics	35
3 Magnetization and assembly	46
E. Applications	47
References	56
2 Intrinsic magnetic properties <i>J. J. M. Franse and R. J. Radwański</i>	58
A. Experimental methods	64
1 Single-crystal growth of $R_2T_{14}B$ compounds	64
2 Magnetization and magnetic susceptibility	64
3 Neutron studies	78
4 Mössbauer and NMR spectroscopy	81
5 Other magnetothermal effects	85
B. 3d Magnetism in $R_2T_{14}B$ and related compounds	87
1 Magnetic moment of the 3d sublattice with non-magnetic rare-earth elements	90
2 Curie temperature	93
3 Magnetovolume effect	95
4 Magnetocrystalline anisotropy energy of the 3d sublattice	95
5 High-field susceptibility	98

xiv

Contents

6 3d magnetic moment in $R_2T_{14}B$ compounds with magnetic rare-earth elements	98
C. $R_2Fe_{14}B$ and related compounds with magnetic rare-earth elements	99
1 $R_2Fe_{14}B$ compounds	99
2 $R_2(Fe, T)_{14}B$ solid solutions	123
3 R_2Fe_{17} and related interstitial compounds	134
4 $R(Fe_{12-x}M_x)$ and related interstitial compounds	143
References	151
3 Phase relations <i>K. G. Knoch</i>	159
1 Binary systems	161
2 The ternary Nd-Fe-B system	163
3 Quaternary systems; additions to Nd-Fe-B	167
4 Additions to Sm-Fe	172
References	174
4 Interstitial modification <i>R. Skomski</i>	178
A. Introduction	178
1 Statistical mechanics of gases in metals	184
B. Nitrides, carbides, and hydrides	189
1 Gas-solid solutions	189
2 Interstitial diffusion	196
3 Interaction effects	200
C. Properties of interstitial permanent magnets	206
1 Magnetic properties	206
2 Processing-related properties	211
References	215
5 Coercivity <i>D. Givord and M. F. Rossignol</i>	218
A. Basic ideas: The single grain as a model system	219
1 Ideal homogeneous material	219
2 Real heterogeneous material	224
B. Theoretical description	225
1 Magnetic parameters	226
2 Models	227
3 Numerical micromagnetic investigations	242
C. Experimental analysis of magnetization reversal in R-Fe-B magnets	247

Contents

xv

1	The $R_2Fe_{14}B$ hard magnetic phase	247
2	Sintered R-Fe-B magnets	249
3	R-Fe-B magnets prepared from ribbons	275
4	Some remarks about other magnets	278
D.	Conclusion: the coercivity mechanisms in R-Fe-B magnets	280
References		283
6	Microstructure and magnetic domains <i>G. Hadjipanayis</i>	286
A.	Experimental techniques	288
1	Electron microscopy imaging and diffraction	288
2	Magnetic domain studies	290
3	A typical microstructure study	294
B.	Studies of specific magnets	295
1	Precipitation-hardened rare-earth magnets	295
2	Rare-earth-iron magnets	298
3	Rare-earth-iron-boron magnets	303
4	Rare-earth-iron carbides	319
5	Alloys with the $ThMn_{12}$ -type structure	320
6	Interstitial rare-earth-iron nitrides and carbides	321
7	Exchange hardened magnets	325
References		329
7	Magnet processing <i>I. R. Harris</i>	286
A.	Nd-Fe-B	336
1	Alloy production	336
2	Monocrystalline powder processing	340
3	Polycrystalline powder processing	353
4	Casting and hot-working	365
B.	Sm-Fe-N	370
References		373
8	Static applications <i>H. A. Leupold</i>	381
A.	Magnetic circuit design	382
1	Magnetic analogue of Ohm's law	382
2	Example of magnetic gap field calculations	387
3	Flux confinement by cladding	391
4	Clad permanent-magnet solenoids	395
B.	Structures composed entirely of rigid permanent magnets	401
1	Linear structures	401
2	Polygonal cavities	405

★

xvi	<i>Contents</i>	12
	3 Rod ensembles	413
	4 Three-dimensional structures	414
	5 Periodic permanent-magnet stacks	419
	References	427
9	Magnetomechanical devices <i>J.-P. Yonnet</i>	430
	A. Forces exerted between permanent magnets	430
	1 Calculation by the Coulombian method	431
	2 Calculation with the dipolar model	436
	B. Permanent-magnet bearings	440
	1 Bearing operation principle	440
	2 The stability of permanent-magnet suspensions	441
	3 Bearing configurations	443
	4 Bearing calculations	445
	5 Uses of permanent-magnet bearings	447
	C. Permanent-magnet couplings	448
	1 Coupling configurations	448
	2 Calculation of permanent-magnet coupling	449
	3 Magnets for couplings	450
	References	450
10	Permanent-magnet motors <i>R. Hanitsch</i>	452
	A. Material properties	452
	1 Magnetic parameters	454
	2 Non-magnetic parameters	457
	3 Corrosion	458
	B. Electrical machines	459
	1 DC machines	459
	2 Synchronous machines	478
	3 Micromotors	489
	4 Magnetization and assembly	491
	References	495
11	Actuators <i>D. Howe</i>	498
	1 Basic principles	500
	2 Application studies	503
	References	512
	Formula Index	513
	Subject Index	515

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348

*I. R. Harris***Table 7.3** Coating procedures for Nd-Fe-B sintered magnets

Coating materials	Technique
Aluminium	Ion vapour deposition
Electropaint	Cathodic
Titanium nitride	Plasma assisted physical vapour deposition
Silicon oxide	Chemical vapour deposition
Nickel/zinc	Electroplating or electroless plating
Zinc	Dacromet process*
Resin coating	Air spray of bulk material, barrel painting

* Coating in an aqueous dispersion containing zinc flakes, chromium and proprietary organics. This is followed by furnace drying to remove water and final baking at 300 °C.

passivation of the particle surface and produces sintered magnets with squarer loop shapes compared with the nonoxygen-treated powder. Magnets made from atomized powder are found to have a finer, more uniform grain size compared with those of a number of other types, and they exhibit very square demagnetization loops [War89].

A variation of atomization which has been used to produce Nd-Fe-B layers is liquid dynamic compaction (LDC) [Chi86, Tan86]. A stream of molten alloy converted into a spray of fine particles by a jet of high-velocity gas is collected on a substrate and a solid layer of Nd-Fe-B is built up. Disadvantages of the technique are that the layer is isotropic, with a large variation in the grain size with depth.

Atomized powder has been encapsulated in a steel container and then extruded at high temperatures [Cha89]. The extruded rods exhibited a radial texture and were subject to an optimizing heat treatment at 900–950 °C, where slight grain growth improved the loop squareness. A field of 2.8 MA/m was required to magnetize the material to an optimum condition. The radial texture is most suitable for permanent magnet motors for electrical machines, as shown in Fig. 7.12. A variant of the process is back extrusion, where the powder is pressed down a central hole and forced back into the space between two coaxial cylinders, where it forms a radially oriented ring magnet suitable for cutting into arc segments. This process has also been applied to melt-spun material (see later).

2.2.2 Hydrogen decrepitation (HD) The use of hydrogen in the processing of rare-earth magnets was first proposed by Harris and coworkers in 1979 [Har79]. Early work concerned hydrogen decrepitation of SmCo₅, but the process was later

15

Magnet processing

349

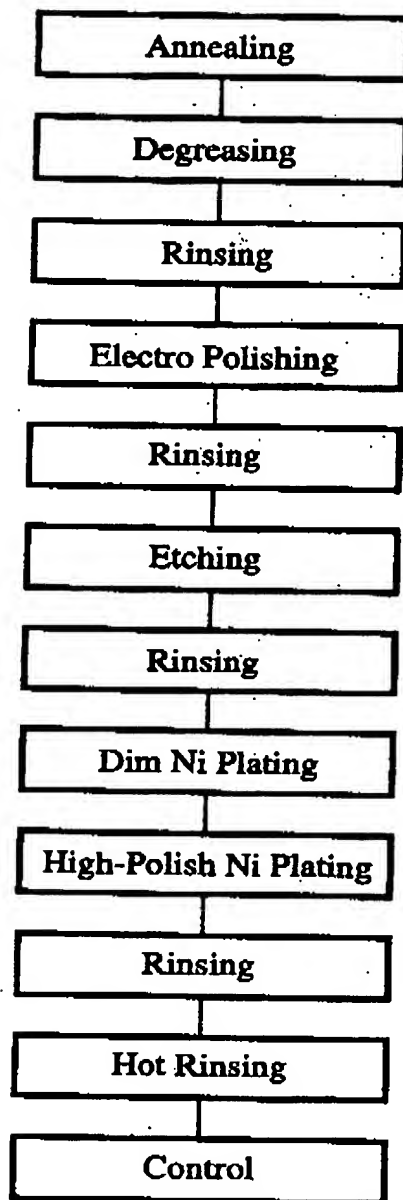


FIG. 7.10. A schematic representation of the nickel coating procedure.

extended to $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_{17}$ -type alloys [Kia84, 85]. Soon after the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, studies showed that alloys such as $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ reacted readily with hydrogen at moderate pressures in a strongly exothermic reaction which led to decrepitation of the ingot [L'He84, Oes84, Har85, 89, Cad86, Wie87, Fru89]. The process has been exploited [McG86, 89b] to produce sintered magnets with excellent properties and the overall process is shown in Fig. 7.13.

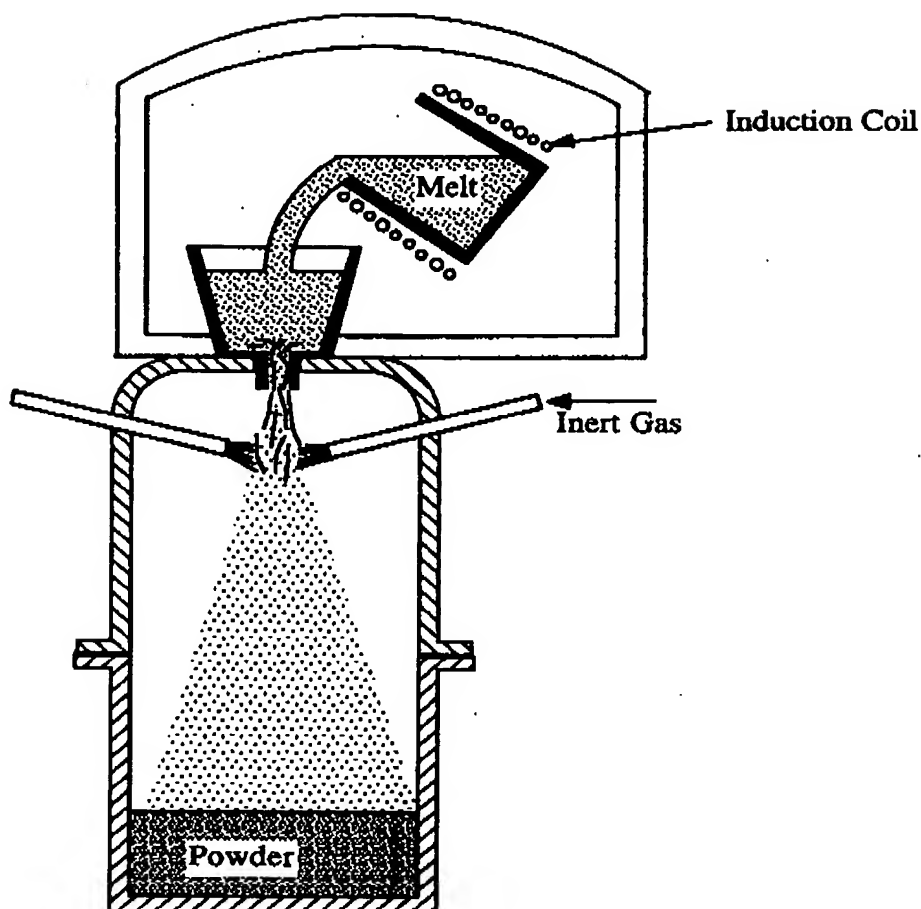


FIG. 7.11. A schematic representation of the atomization process.

Although hydrogen lowers the anisotropy field of $\text{Nd}_2\text{Fe}_{14}\text{B}$, [Oes84] the hydrided powder is still sufficiently anisotropic for the c -axes of the crystallites to be aligned effectively by a modest magnetic field of 1 T. The hydrogen is then removed from the alloy during a vacuum anneal prior to sintering. Figure 7.14 shows that hydrogen is desorbed in three stages [Wil90, 91, Nak90], first from the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase and then in two steps from the Nd-rich phases. Benefits of hydrogen decrepitation are numerous. The major advantage is that the normally tough induction-melted ingots can easily be reduced to a relatively fine powder which is extremely friable. This means that the jaw crushing and coarse milling operations, which are difficult and expensive in energy, can be eliminated, and the time for jet milling can thus be reduced considerably (Fig. 7.15). Intergranular failure produces single-crystal particles with very clean surfaces which are ideal for sintering, and it is possible to control the particle size and shape distribution by varying the HD conditions. Oxygen pick-up during processing is reduced as desorption of hydrogen

Magnet processing

351

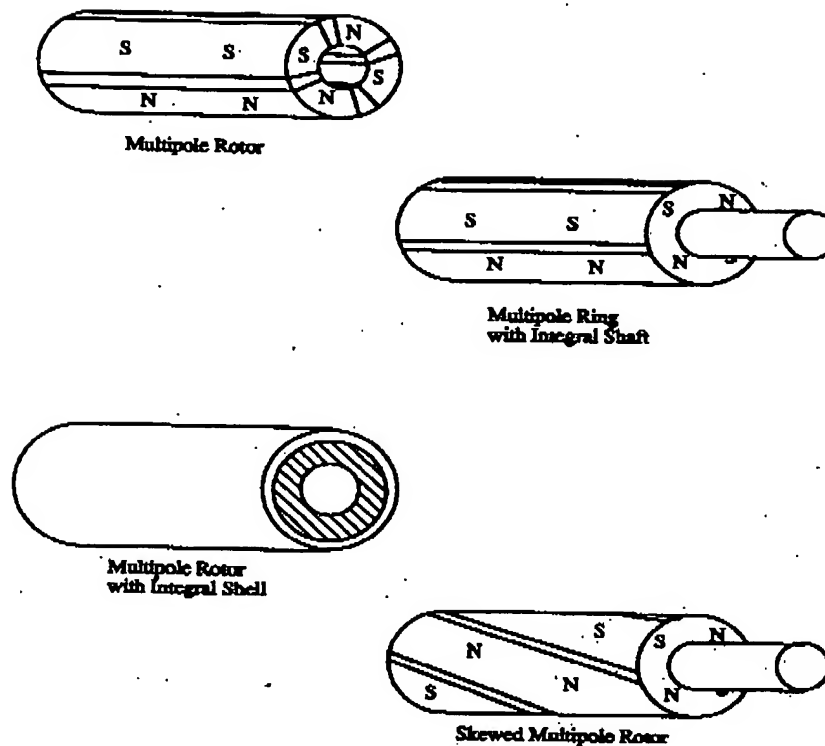


FIG. 7.12. Various forms of extruded rods using atomized powder for electric motor applications.

on heating the green compacts creates a nonoxidizing environment. The near-zero remanence of the compacts makes them easy to handle.

The morphology of the hydrided material [McG90a, 90b], together with a typical particle-size distribution, are shown in Fig. 7.16. Flake-like powder is often produced by an 'onion skin' decrepitation mechanism. Thus, hydrogen diffuses into the bulk to a particular depth below the surface where a critical strain resulting from the volume difference between the hydrided and nonhydrided material causes fracture at the interface and hence flaking. This fracture behaviour is characteristic of tough material such as ingot-containing dendritic α -Fe (Fig. 7.2). Homogenized ingots exhibit different hydrogen decrepitation behaviour [McG90c], with a faster reaction rate and evidence of intergranular and transgranular failure more typical of the HD-behaviour of 2:17 alloys [Kia85].

The hydrogen decrepitation process can be applied in the manufacture of the whole family of Nd-Fe-B alloys, and it has been adopted by magnet manufacturers throughout the world. Their magnets tend to have finer grain size and hence greater mechanical strength than the magnets produced by the conventional powder process. The HD process has also been employed to produce coercive powder from hot-pressed, die-upset and hot-rolled material, and these processes will be described later in the chapter.

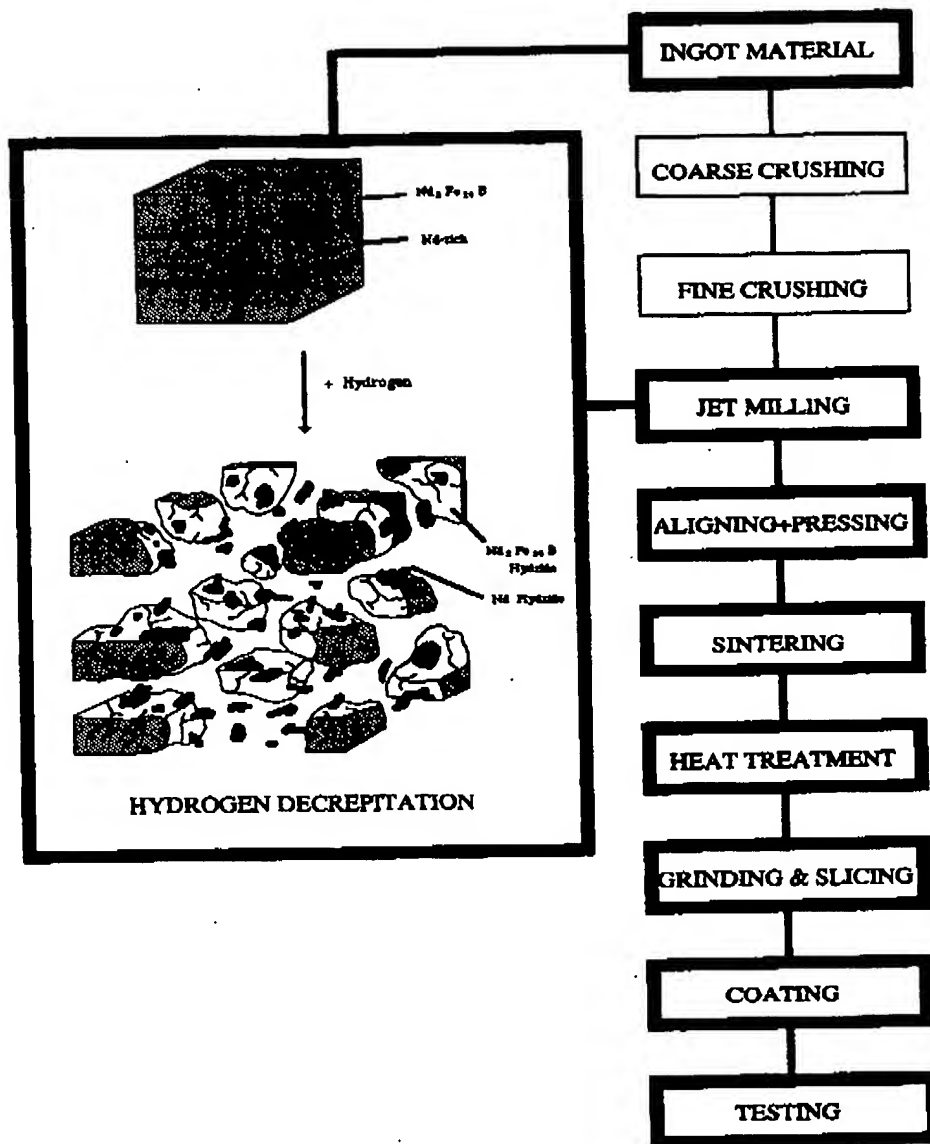


FIG. 7.13. The hydrogen decrepitation (HD) process.

Hydrogen has also been employed to characterize Nd-Fe-B-type ingots, powders and sintered magnets. Thus the hydrogen uptake [Cad86, Har87a, b, c, 89, Scho87] enthalphy of hydrogen absorption [Har87a, b, c, Scho87, McG89c] and the thermal desorption behaviour [Har87a, b, c, 90, Scho87, Rup88, McG89c, Nak90, Wil90, 91] can be used to determine the proportion of Nd-rich material in a particular sample and the extent of oxidation of this material.

Magnet processing

353

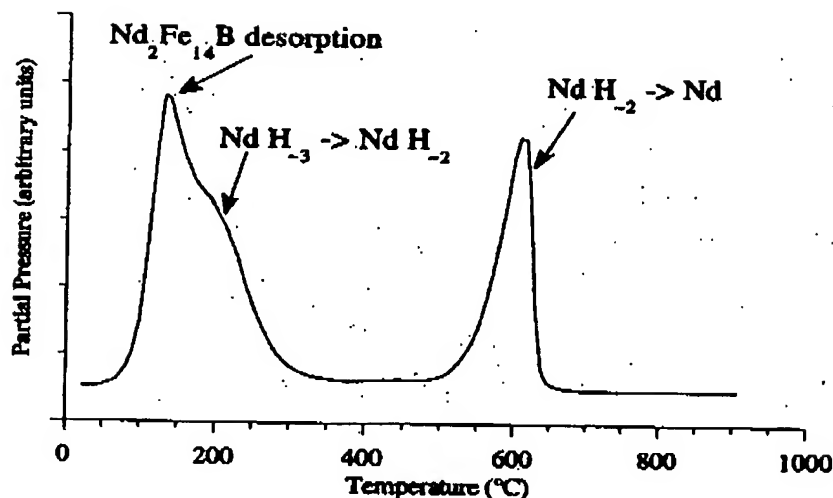


FIG. 7.14. Mass spectrometer trace of the hydrogen desorption behaviour of hydrided $\text{Nd}_{16}\text{Fe}_7\text{B}_8$ powder.

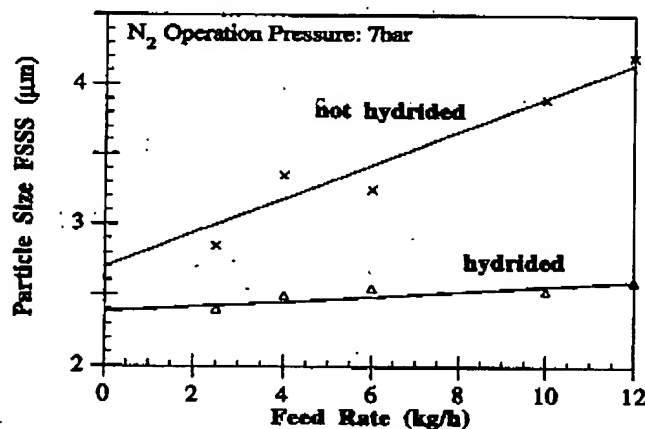


FIG. 7.15. Particle size of jet milled powder (determined by Fisher Sub Sieve Sizer, FSSS) vs feed rate for hydrided and nonhydrided feedstock.

3 Polycrystalline powder processing

There are three main independent methods of processing Nd-Fe-B into coercive particles where each particle is constituted by many submicron grains which may be contiguous or separated by a grain-boundary phase. This material can be mixed with epoxy resin or rubber and moulded into appropriate shapes, or combined with a thermoplastic polymer such as nylon and used as a feed stock for injection moulding of complex net-shape components. Many polymer-loaded magnets are

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Magnet processing

361

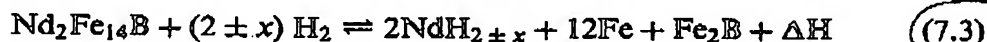
min, which yields a grain size of around 50 nm. Resin-bonded magnets exhibiting isotropic properties can be made from this material and compacted magnets can be made by hot uniaxial pressing. Magnetically anisotropic magnets can be prepared by die-upset forging at high temperatures with process conditions similar to those employed for the melt-spun ribbon.

3.3 The hydrogenation, disproportionation, desorption and recombination (HDDR) process

Coercive powder can be produced from the cast and homogenized Nd-Fe-B-type ingots by the HDDR-process, and this is illustrated in Fig. 7.20. When Nd-Fe-B alloys are heated in hydrogen to above 650 °C, the Nd₂Fe₁₄B matrix phase disproportionates into iron, neodymium hydride and ferroboron [L'He84, Har85, Oes85, Cad86] and in 1985, Oesterreicher [Oes85] proposed that it should be possible to recombine such a disproportionated mixture by heating under vacuum, thus producing a fine grained microstructure, as observed previously for hydrogen storage alloys.

In 1989, Takeshita and Nakayama [Tak89] reported that coercive powder could be produced by heating Nd-Fe-B alloys under hydrogen and then vacuum annealing. McGuinness and coworkers [McG90a, 90b] interpreted this behaviour in terms of what they termed a hydrogenation, disproportionation, desorption and recombination (HDDR) reaction.

The disproportionation reaction can be represented as:



ΔH is the exothermic (absorption) or endothermic (desorption) heat of reaction. The particular value of x depends on the temperature and hydrogen pressure.

The disproportionated mixture (see Fig. 7.20) consists of a very finely divided mixture of the components [Kia92, Gut94a, 94b, Mar94, Mar94] and on removal of the hydrogen by vacuum annealing, the Nd, Fe₂B and Fe recombine to form Nd₂Fe₁₄B with a submicron ($\sim 0.3 \mu\text{m}$) grain size. Thus the HDDR process converts the initial, coarse grained ingot material (Fig. 7.2) into very fine grained powder (Fig. 7.20), which, if optimally processed, exhibits appreciable intrinsic coercivity. The best magnetic properties for the HDDR powder are achieved by an annealing treatment which leads to an Fe-free, uniformly fine grained ($\sim 0.3 \mu\text{m}$) microstructure. Too low an annealing temperature results in the persistence of α -Fe, whereas too high a temperature results in the rapid growth of large faceted grains [Har92, McG92, Jon94]. Both these features are inimical to the development of coercivity. These microstructures are illustrated in Fig. 7.21.

Takeshita and coworkers [Tak90, 92, Nak93] have shown that small additions of certain elements such as Zr, Hf or Ga (e.g. Nd_{12.5}Fe_{69.9}Co_{11.5}B_{6.0}Zr_{0.1}) have the remarkable effect of producing anisotropic HDDR powder from which resin-bonded magnets with $(BH)_{\text{max}}$ values around 140 kJ/m³ have been produced [Tak90, 92, Nak93, 94]. According to Nakayama *et al.* [Nak94], it was necessary to homogenize the alloys at 1120 °C for 20 h in 1 bar argon. They were then crushed into blocks of size less than 20 × 20 × 20 mm³, then heated in hydrogen at 1 bar to

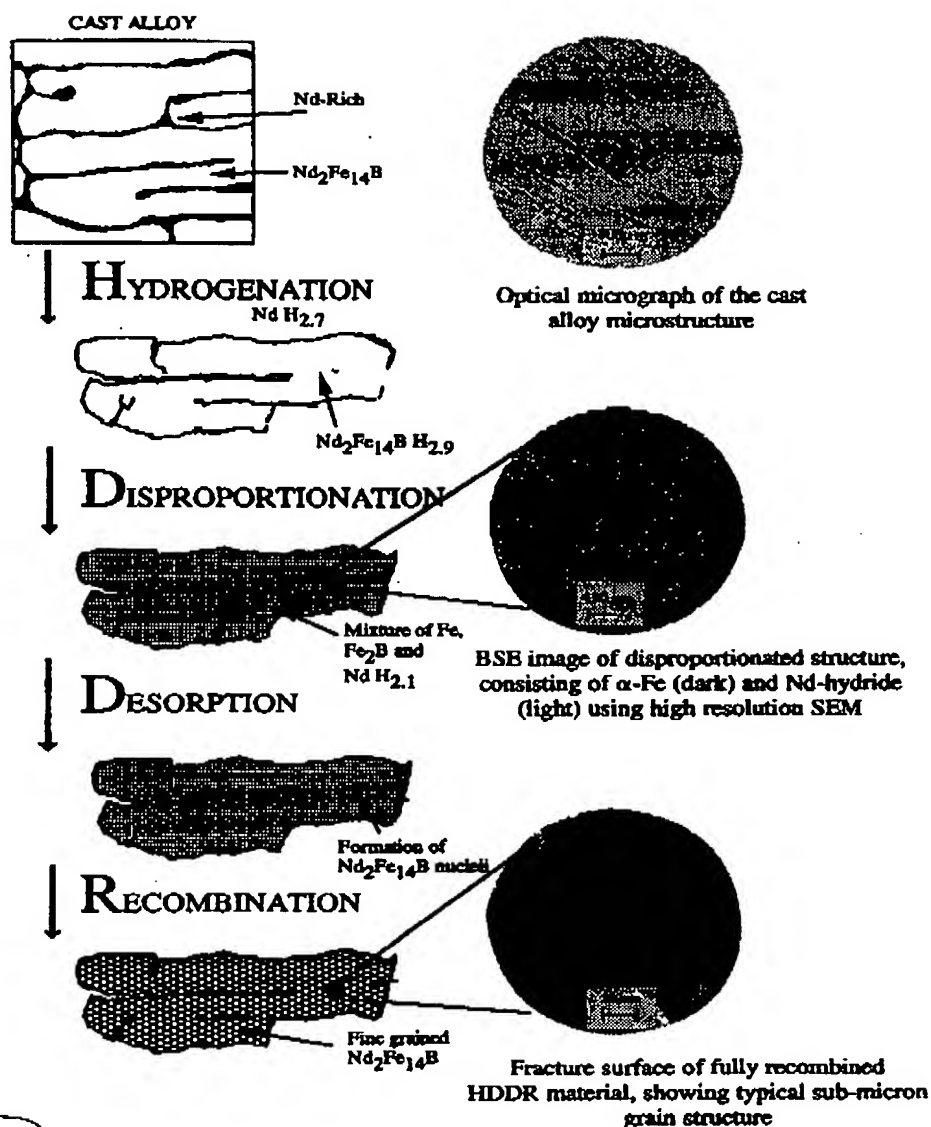


FIG. 7.20. A schematic representation of the HDDR process with typical microstructures.

830 °C and kept at this temperature for 10 min. The system was then evacuated to a high vacuum ($\sim 10^{-8}$ bar) for about 40 min and the material was subsequently quenched in argon gas. The anisotropic bonded magnets were prepared by mixing the HDDR powder (crushed to a particle size of $< 420 \mu\text{m}$) with epoxy resin and moulding in an alignment field of 2.5 T. The magnets were then set by heating at 100 °C for 2 h.

The HDDR powder has also been found to be very suitable for the production of hot-pressed magnets [Har92, McG92, Tak92, Manw94]. The hot-pressed magnets reported by McGuinness *et al.* [McG92] and by Manwaring and coworkers [Man94]

22

Magnet processing

363

(a)



(b)

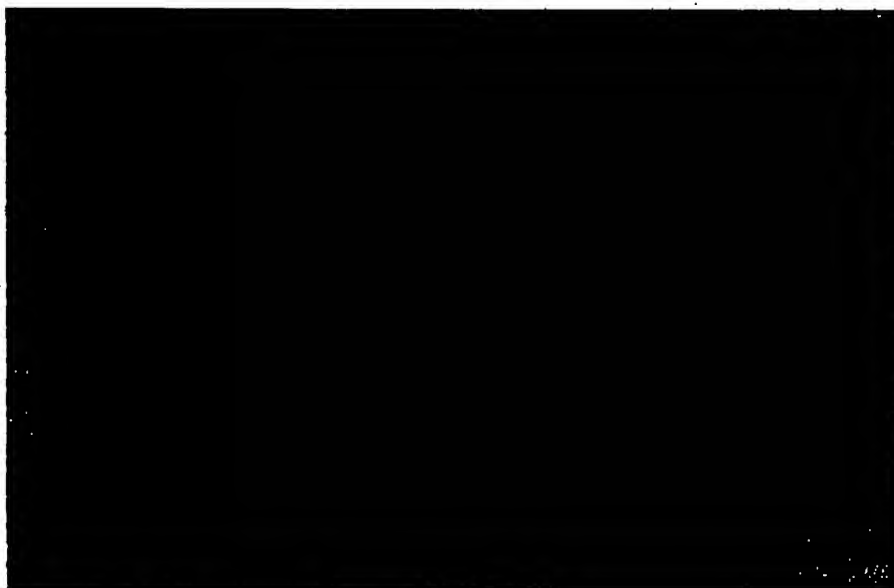




FIG. 7.21. The microstructure of an HDDR particle (a) below optimum processing temperature showing the presence of α -Fe dendrites; (b) at optimum temperature showing uniform fine grain size; (c) above optimum temperature showing the presence of large faceted grains coexisting with very fine grains.

were produced by making a green compact of ~ 7 gm using coarse ground isotropic HDDR powder. The green compacts were then pressed by 790°C using a load of 2 tonnes/cm^2 until full density had been obtained. Hot-pressed magnets based on the composition $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ exhibited $B_r \approx 0.8\text{ T}$, $H_c \approx 1160\text{ kA/m}$ and $(BH)_{\text{max}} \approx 108\text{ kJ/m}^3$ and the enhanced value of B_r for this composition indicated a degree of upsetting during the hot-pressing operation. Electron microscope observations [Est94] of these magnets indicated an average grain size of $\sim 0.4\text{ }\mu\text{m}$, which means that the enhanced remanence could not be ascribed to exchange coupling. Die-upset forging experiments by McGuinness *et al.* [McG92] indicated that the hot-pressed HDDR compacts ($\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$) exhibited a rate of increase of B_r with an upset ratio very similar to that observed by Tokunaga *et al.* [Tok89] for melt-spun compacts based on ($\text{Nd}_{14}\text{Fe}_{80}\text{B}_6$). The coercivities of the HDDR magnets, however, exhibited a much smaller decrease with upset ratio than those of the melt-spun magnets.

It is possible to avoid decrepitation of the alloy during the HDDR processing by introducing the hydrogen at or above the minimum disproportionation temperature. This has been called the S(solid)-HDDR process [Gut94a, 94b]. Rapid heating of a near-stoichiometric alloy ($\text{Nd}_{2.1}\text{Fe}_{14}\text{B}$) in a hydrogen

Magnet processing

365

atmosphere also avoids decrepitation [Zba91]. A useful consequence of the HDDR process is that it is a very effective means of homogenizing near-stoichiometric compositions which contain α -Fe dendrites in the cast state [Har92]. The α -Fe can be removed quickly compared with standard homogenization treatment by annealing the alloy in the disproportionated state at a relatively modest temperature ($\approx 750^\circ\text{C}$).

4 Casting and hot-working

One of the most cost-effective means of producing anisotropic, fully dense Nd-Fe-B magnets would be to cast them into slabs with a fine grain size and with the *c*-axis of the grains aligned perpendicular to the surface of the slab. In the case of Pr-Fe-B-Cu alloys, appreciable coercivities (up to 1070 kA/m) can be obtained in the cast condition [Shi88a, Far91, Myc93]. Unfortunately, the orientation is such that there is a more or less random *c*-axis orientation in the plane at right angles to the predominant cooling direction, so that it is not possible to produce highly aligned anisotropic magnets from the cast material without subsequent hot deformation. Isotropic cast magnets based on Nd₂Fe₁₄C can be produced [Bus88, Gri91, Fri94] simply by casting, for example, a Nd-Fe-Cu-C-B alloy and then subsequently annealing between 900 °C and 950 °C for 5-6 days, during which time fine grain Nd₂Fe₁₄C is formed by a very slow solid-state reaction. By this means it is possible to produce magnets with $B_r \approx 0.61$ T, $H_c \approx 600$ kA/m and $(BH)_{\max} \approx 61$ kJ/m³. To obtain magnets from cast material with much higher $(BH)_{\max}$ values it is necessary to subject the alloys to a hot deformation process. Because of the necessary scale of the operation to make them economical, these processes are usually hot-extrusion or hot-rolling. In the Nd-Fe-B (and Pr-Fe-B) alloys containing excess rare-earth, the processes are much aided by the presence of an intergranular liquid phase at the deformation temperature.

The first report of a direct mechanical method of making Nd-Fe-B magnets from cast material was by Ervens [Erv89], who extruded rods at 800 °C which exhibited a radial magnetic orientation. The magnetic properties were found to depend upon the extrusion conditions such that higher remanence with a lower coercivity appeared at lower extrusion velocities. Unfortunately, these magnets were unstable and there was an irreversible loss in the coercivity even on standing at room temperature.

The extrusion process was much improved by Nozières and coworkers [Noz89a, 89b, 90], who encapsulated the Nd-Fe-B alloy in an iron sheath which was capped and sealed by welding in an inert atmosphere in order to prevent oxidation and loss of the liquid phase during extrusion. The bar was then extruded at temperatures in the range 750-850 °C and a high deformation ratio (> 10) was required to achieve a pronounced radial texture. A final anneal was needed to optimize the magnetic properties. Metallographic studies of the extruded bar showed that the mechanical working resulted in a decrease in the average grain size to around 0.5-10 μm , with the NdFe₄B₄ phase strung out along the hot-working direction. The radially